



Interaction of tannic acid with ferric iron to assist 2,4,6-trichlorophenol catalytic decomposition and reuse of ferric sludge as a source of iron catalyst in Fenton-based treatment

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ABSTRACT

A comprehensive study of the catalytic behaviour of Fe^{3+} in the presence of tannic acid during the Fenton-based treatment of chlorophenols-contaminated water was performed. The ability of the iron-containing sludge to catalyse the Fenton-based process was assessed and the mechanistic behaviour of tannic acid in the iron dissolution was evaluated.

Tannic acid, a constituent of pulp and paper industry water effluent and natural water, enhanced the 2,4,6-trichlorophenol catalytic decomposition in Fe^{3+} -activated H_2O_2 oxidation system by reducing of the Fe^{3+} . The Fe^{3+} reductive mechanism by tannic acid incorporated tannic acid- Fe^{3+} complex formation and decay through an electron transfer reaction to form Fe^{2+} . An indirect measurement of hydroxyl radical (HO^\bullet) by the deoxyribose method indicated a considerable increase in HO^\bullet by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ in the presence of tannic acid. A pseudo-first reaction rate constant of 2,4,6-trichlorophenol degradation by $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ was high and close to that of $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ with tannic acid. Degradation of tannic acid along with that of 2,4,6-trichlorophenol required optimization of H_2O_2 and Fe^{3+} dosages to balance HO^\bullet formation and scavenging.

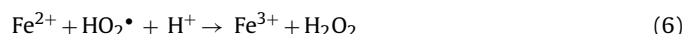
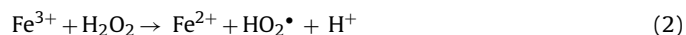
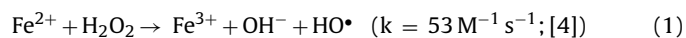
Acidic reaction media (pH 3.0) and the presence of tannic acid favoured 2,4,6-trichlorophenol degradation by H_2O_2 oxidation induced by iron dissolved from ferric oxyhydroxide sludge. The reuse of ferric oxyhydroxide sludge as a catalyst source in the Fenton-based process can minimise the production of hazardous solid waste and the overall cost of the treatment.

This study highlights the ability of tannic acid- Fe^{3+} complexes to participate in Fe^{3+} reductive pathway and, as a result, to allow reuse of non-regenerated ferric oxyhydroxide sludge for activation of H_2O_2 oxidation in wastewater treatment at acidic pH.

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1. Introduction

Degradation by many advanced oxidation processes involves the oxidative reactions of highly reactive hydroxyl radicals (HO^\bullet) with target organic compounds. In Fenton treatment, transition metals ions, such as the ferrous ion (Fe^{2+}), play a key role in the activation of hydrogen peroxide (H_2O_2) oxidation of organic contaminants to promote the formation of HO^\bullet (Eqs. (1)–(7)) [1–3].



In general, the reaction of ferric iron (Fe^{3+}) with H_2O_2 (Eq. (2)) is several orders of magnitude slower than Reaction (1), and thus Reaction (2) can become the rate-limiting step. However, other important reactions with iron ions in Fenton chemistry influence the overall degradation rate substantially. In these reactions, organic compounds may act as ligands (L) to form complexes with iron ions, or act as redox agents resulting in the autocatalytic transformation of iron catalyst. Possible interactions include (1) photolysis of Fe^{3+} -L complexes, (2) formation of reactive high valent iron-oxo or iron-peroxo complexes that are stabilized by

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L, (3) reduction of Fe^{3+} by neutral organic molecules or organic radicals, and (4) oxidation of Fe^{2+} by radicals or carbo-cations [5].

A number of variations of the Fenton reaction has been studied, including those using Fe^{2+} and Fe^{3+} with the supplementary addition of complexing ligands (Interaction (2)) [6,7] or reductants (Interaction (3)) [8,9]. Little is known, however, about the influence of target compounds (treated water constituents) or their degradation by-products [10] on the reactivity of iron.

Chlorophenols are listed as priority pollutants [11] and have been found to be toxic to aquatic environments [12]. They are formed as undesirable by-products of many industrial processes—such as, disinfection of drinking water, production of paper, waste incineration, cooking process and coal pyrolysis—that involve organic compounds and chlorine. Studies on the state of environmental pollution confirm the presence of chlorophenols in surface and ground water, bottom sediments, atmospheric air and soil [13]. Tannins are plant-based polyphenolic compounds that are found in natural water and are known to be bioreistant [14] and toxic to bacteria and fish [15,16]. Chlorophenols and tannins are both found in pulp and paper industrial effluent [17] and natural water [13,18].

Studies on the effective treatment of chlorophenol-containing effluent are significant since large volumes of wastewater are produced. The most widely used treatment method, bio-oxidation, is unable to remove toxic organic pollutants such as chlorophenols completely from wastewater [19]. Based on the principle of best available technique, the use of additional treatment steps is usually required to provide the highest effluent quality. Fenton treatment is applied successfully in sequential mode as a preliminary step in pulp and paper industrial effluent treatment followed by a biological process [20]. This strategy relies on the principle that recalcitrant pollutants tend to be more reactive chemically than biologically, whereas the opposite is typical for their degradation by-products. The Fenton-based process was found to be effective for chlorophenol- [21–24] and tannin-contaminated water [25] and pulp and paper industry effluent [20,26] treatment.

Despite Perez et al. [26] findings that Fenton and photo-Fenton reactions were highly effective for pulp and paper water effluent treatment, practical applications of Fenton-based treatment processes may be limited by sludge generation. Fe^{3+} formed in Reactions (1), (4), and (6) is known to precipitate as amorphous ferric oxyhydroxide (undesirable (ferric) sludge in technological applications) with increases in pH from strongly acidic to neutral. In our previous study [27], wastewater from different industrial sites, including tannins-containing wood-soaking basin effluent from a plywood manufacturing plant was subjected to Fenton-based treatment using non-regenerated ferric sludge as activator. Although the application of this method resulted in a substantial reduction in treated wastewater chemical oxygen demand, a study of activation mechanism of the H_2O_2 oxidation with ferric sludge was not performed. Studies of the catalytic behaviour of Fe^{3+} in wastewater are usually limited because of the matrix complexity. In a study that tested the ability of ascorbic acid to improve Fe^{3+} activation of alachlor Fenton-like oxidation [9], it was assumed that some wastewater constituents and their degradation by-products are similar to ascorbic acid in organic radical formation and in the reduction of Fe^{3+} to Fe^{2+} by electron transfer. The effect of reductive agent, hydroxylamine, in assistance of Fe(III)/Fe(II) redox cycle on the iron-loaded natural zeolite surface and enhancement the generation of HO^\bullet via decomposition of H_2O_2 was observed in the study of Fukuchi et al. [8]. Non-regenerated ferric sludge may therefore be reused for the activation of H_2O_2 oxidation in wastewater treatment at acidic pH.

Tannins are strong transition metal-chelating [28] and -reducing [29] agents. They exhibit antioxidation (act as HO^\bullet

scavengers) [30] and pro-oxidation (promote HO^\bullet generation in the presence of transition metals) [31] properties in biological systems (living organisms). Thus, the presence of tannins in the reaction mixture may hypothetically influence the efficacy of Fenton treatment by promoting the ability of iron ions by Interactions (2), (3) to activate oxidation. In the study of Rodriguez et al. [32], the supplementary addition of catechols, compounds that possess similar transition metal-reducing properties [33] to those of tannins, to pulp-bleaching effluent increased the fraction of organo-halogen compounds that was removed in the Fenton-based process. Chlorophenols degradation by-products as quinone- and hydroquinone-structure compounds [33–35] may assist the Fenton oxidation by reducing Fe^{3+} to Fe^{2+} or acting in the form of semiquinone radicals as electron-transfer catalysts between the dihydroxycyclohexadienyl radical (HO^\bullet adduct of phenol) and Fe^{3+} [5].

Although the Fenton-based process is an essential contributor to chlorophenol oxidative transformation in natural water [13], its mechanism is still under discussion, since many factors in the natural environment, such as matrix composition, pH, and temperature influence the reaction pathway. Iron is among the most abundant elements of natural water that is involved in many redox reactions including with H_2O_2 and organic compounds. The effect of tannins that are also found among constituents of natural water on the Fe^{3+} reduction and the Fenton-based process efficacy is of notable interest. Nevertheless, studies on mechanistic behaviour of tannic acid in the Fenton-based processes have not been reported.

In this research, the ability of tannic acid (TN) to interact with Fe^{3+} , promote the activation of H_2O_2 oxidation of 2,4,6-trichlorophenol (TCP), and assist reuse of ferric sludge as a source of iron catalyst in wastewater Fenton-based treatment was assessed. TCP degradation, the dechlorination, HO^\bullet production, and H_2O_2 consumption in $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ in the presence and absence of TN and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ were studied. The mechanistic behaviour and ability of TN to form complexes and to reduce Fe^{3+} at pH 3.0 were evaluated. This study on the influence of water constituents on Fe^{3+} to Fe^{2+} reduction contributes substantially to Fenton-based treatment efficacy and creates a hypothesis for studies on chlorophenols transformation routes in the presence of TN in natural water. The novelty of the study is the understanding of the mechanism of the sludge reuse for the Fenton oxidation in the presence of the reductive agents as TN a major constituent of the wastewater.

2. Materials and methods

2.1. Reagents

All chemicals used were of analytical grade. TCP ($\text{Cl}_3\text{C}_6\text{H}_2\text{OH}$, $\geq 97\%$), TN ($\text{C}_{76}\text{H}_{52}\text{O}_{46}$, ASC grade reagent), ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\geq 99\%$), ferric sulphate nonahydrate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, $\geq 99\%$), hydrogen peroxide (H_2O_2 , $\geq 30\%$ w/w), 2-deoxy-D-ribose ($\text{C}_5\text{H}_{10}\text{O}_4$, $\geq 99\%$), 2-thiobarbituric acid ($\text{C}_4\text{H}_4\text{N}_2\text{O}_2\text{S}$, $\geq 98\%$), trichloroacetic acid (Cl_3CCOOH , $\geq 99\%$), and 1,1,3,3-tetraethoxypropane ($((\text{C}_2\text{H}_5\text{O})_2\text{CHCH}_2\text{CH}(\text{OC}_2\text{H}_5)_2$, $\geq 96\%$) were purchased from Sigma-Aldrich. Solutions were prepared using ultrapure water obtained from a Millipore ultrapure water UV-system (Simplicity[®], EMD Millipore Corporation, Billerica, MA, USA).

2.2. TCP-spiked water treatment

Treatment of a $10\ \mu\text{M}$ TCP aqueous solution (1 L) with $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, $\text{Fe}^{3+}/\text{H}_2\text{O}_2$, ferric sludge/ H_2O_2 , and H_2O_2 was performed in a batch reactor at ambient temperature ($21 \pm 1^\circ\text{C}$) and under acidic conditions (pH 3.0). The initial concentrations of H_2O_2

were 100 and 400 μM , which corresponds to a TCP/ H_2O_2 molar ratio of 1/10 and 1/40, respectively. The molar ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ was maintained at 1/10, which is close to that of 1/11 predicted theoretically for 2,4-dichlorophenol degradation by Tang and Huang [21]. Two initial concentrations of 10 and 50 mg L^{-1} TN were tested. These concentrations were indicative of TCP and TN concentrations found in pulp and paper (bleached kraft) mill effluent [36]. Solution pH was adjusted using a 0.5 M sulfuric acid or 0.1 M sodium hydroxide solution. The oxidation process was initiated by simultaneous addition of Fe^{2+} , or ferric sludge and H_2O_2 to TCP solution with the previously added TN (if required). The reaction mixture was mixed continuously using a multiple magnetic stirrer. Oxidation was stopped by 0.1 M Na_2SO_3 solution addition (1/2, v/v). Ferric sludge was synthesized by mixing sodium hydroxide and ferric sulphate solutions with further filtration and washing out of sodium sulphate from precipitate. Dried sludge (50 mg) was added to the treated solution (1 L). The treatment times were 120 min and 300 min for soluble iron/ H_2O_2 and ferric sludge/ H_2O_2 , respectively. For evaluation of the adsorption of TCP to the hydroxide surface the solution of TCP was mixed with ferric sludge for 300 min and the TCP concentration in bulk solution was measured. All samples after ferric sludge/ H_2O_2 treatment were filtered using Millipore (Express® plus, EMD Millipore Corporation, Billerica, MA, USA) membrane filters. All water treatment experiments were duplicated. The standard deviation of the results was less than 5%.

2.3. Analyses

The HO^\bullet concentration was estimated using the deoxyribose method [37]. This method is based on the reaction of HO^\bullet with 2-deoxy-D-ribose to produce an oxidation by-product, malondialdehyde (MDA), which then reacts with 2-thiobarbituric acid (TBA). A 2.8 mM 2-deoxy-D-ribose solution was oxidized by HO^\bullet generated by $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, $\text{Fe}^{3+}/\text{H}_2\text{O}_2$, and $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{TN}$. The reaction mixture pH was kept at 3.0 using a 40 mM $\text{H}_3\text{PO}_4/\text{KH}_2\text{PO}_4$ buffer solution. The reaction was stopped by addition of 1.25 mL of a 2.8% (w/v) trichloroacetic acid solution. TBA (1.25 mL, 1% w/v) was added and the reaction mixture was heated to 90–100 °C for 20 min. The absorbance of resultant pink chromophore (TBA-MDA reaction product) was determined in a 1-cm-pathlength cuvette at 532 nm using a Helios ultraviolet-visible spectrophotometer (Thermo Electron Corporation, Beverly, MA, USA). The HO^\bullet concentration was equated to the TBA-MDA reaction product using an extinction coefficient of $1.56 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ [38]. HO^\bullet production was controlled in the reaction mixtures that contained any of the components, such as TN, H_2O_2 , Fe^{2+} or Fe^{3+} .

Chloride ion (Cl^-) was detected using an ion chromatograph (761CompactIC, Metrohm) equipped with a suppressed conductivity detector and a Metrosep A Supp 5 (150 mm \times 4.0 mm inner diameter) analytical column.

Total iron and Fe^{2+} concentrations in the Fe^{3+}/TN and $\text{Fe}^{3+}/\text{TN}/\text{H}_2\text{O}_2$, and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ systems were measured photometrically at 492 nm using the o-phenanthroline method [39]. H_2O_2 in the reaction mixture was analysed photometrically at 410 nm as a complex of H_2O_2 with Ti^{4+} [40]. Absorption spectra of TN, Fe^{3+} , and the TN- Fe^{3+} complex in solutions prepared under identical conditions to those of the water treatment experiments were recorded between 250 and 700 nm. The TCP concentration in spiked water was measured using a high performance liquid chromatograph (YL-Instrument 9300, Young Lin Instrument Corporation, Hoggie-dong, Anyang, Korea) equipped with a Waters Bridge (150 mm \times 3.0 mm inner diameter) C18 (3.5 μm particle size) column. Light absorbance was measured by ultraviolet-visible photometric detector at 295 nm. Isocratic elution was achieved with 40% eluent A (0.1% CH_3COOH in ultrapure water), and 60% eluent B (acetonitrile) at 0.2 mL min^{-1} . The total analysis time was

Table 1

Pseudo-first order reaction rate constant (k_1 , min^{-1}) of TCP degradation by $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, $\text{Fe}^{3+}/\text{H}_2\text{O}_2$, and ferric sludge/ H_2O_2 with and without TN.

Process	k_1 (min^{-1}), (Treatment time, min)	R^2
TCP/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 1/1/10$	6.3×10^{-2} (0–120)	0.987
TCP/ $\text{Fe}^{3+}/\text{H}_2\text{O}_2 = 1/1/10$	2.1×10^{-3} (0–120)	0.970
TCP/ $\text{Fe}^{3+}/\text{H}_2\text{O}_2 = 1/1/10$	7.2×10^{-3} (0–60)	0.989
[TN] $_0 = 50 \text{ mg L}^{-1}$	4.1×10^{-3} (60–120)	0.993
TCP/ $\text{Fe}^{3+}/\text{H}_2\text{O}_2 = 1/1/10$	4.0×10^{-2} (0–60)	0.995
[TN] $_0 = 10 \text{ mg L}^{-1}$	1.7×10^{-2} (60–120)	0.998
TCP/ $\text{Fe}^{3+}/\text{H}_2\text{O}_2 = 1/4/40$	5.8×10^{-3} (0–40)	0.960
	2.1×10^{-1} (60–90)	0.997
TCP/ $\text{Fe}^{3+}/\text{H}_2\text{O}_2 = 1/4/40$	1.4×10^{-1} (0–30)	0.997
[TN] $_0 = 50 \text{ mg L}^{-1}$	5.1×10^{-2} (30–90)	0.992
TCP/ $\text{H}_2\text{O}_2 = 1/10$	1.2×10^{-2} (0–300)	0.997
[ferric sludge] $_0 = 50 \text{ mg L}^{-1}$		
[TN] $_0 = 10 \text{ mg L}^{-1}$		
TCP/ $\text{H}_2\text{O}_2 = 1/40$	8.7×10^{-3} (0–300)	0.991
[ferric sludge] $_0 = 50 \text{ mg L}^{-1}$		
[TN] $_0 = 50 \text{ mg L}^{-1}$		
TCP/ $\text{H}_2\text{O}_2 = 1/40$	2.7×10^{-3} (0–300)	0.965
[ferric sludge] $_0 = 50 \text{ mg L}^{-1}$		

R—correlation coefficient.

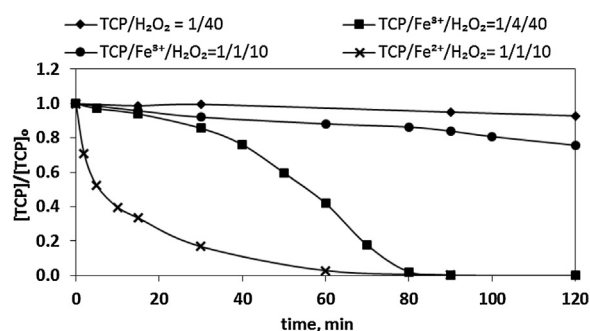


Fig. 1. TCP degradation by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ ([TCP] $_0 = 10 \mu\text{M}$, [Fe^{2+}] $_0 = 10 \mu\text{M}$, [Fe^{3+}] $_0 = 10$ or $40 \mu\text{M}$, [H_2O_2] $_0 = 100$ or $400 \mu\text{M}$) within 120 min treatment.

22 min. The injected sample volume was 20 μL . The detection limit was 0.1 μM TCP.

3. Results and discussion

3.1. TCP degradation by $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ in the absence of TN

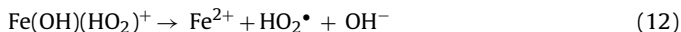
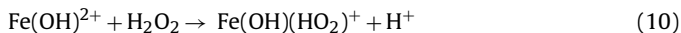
A kinetic study accomplished by path integral analyses of TCP concentration curves versus time indicated that TCP degradation in the Fenton-based processes followed a pseudo-first order kinetic law. The pseudo-first order reaction rate constant (k_1) according to Eq. (8) is calculated from the slope of the straight line by plotting $\ln([TCP]_0/[TCP])$ as a function of time (t) by linear regression.

$$\ln \left(\frac{[TCP]_0}{[TCP]} \right) = k_1 \cdot t \quad (8)$$

Kinetic analyses of TCP degradation curves indicated a multiple-step Fenton-like reaction pathway in some cases, where each step can be characterized by an individual reaction rate constant (Table 1). TCP degradation profiles analysed without suggested multiple-step reaction pathway fit to pseudo-first or pseudo-second kinetics with substantially lower correlation coefficient values.

The degradation of TCP by $\text{Fe}^{3+}/\text{H}_2\text{O}_2 = 1/40$ (M/M) was followed by a lag-phase (Table 1, Fig. 1). $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ is known as a Fenton-like system and is able to oxidize organic compounds. The detailed investigation of Fenton-like system general reaction (Eq. (2)) indicated the formation of $\text{H}_2\text{O}_2\text{-Fe}^{3+}$ complexes (Eqs. (9) and (10))

with their decomposition to hydroperoxyl radicals (HO_2^\bullet) and Fe^{3+} reduction (Eqs. (11) and (12)) [41]. Besides HO_2^\bullet , HO^\bullet can be formed according to the classical Fenton pathway (Eq. (1)).



The $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ process is known to be less reactive than $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ [42] because of a rate-limiting step of the reductive dissociation of the $\text{Fe}(\text{III})$ -peroxo complex (Eqs. (11) and (12)) in the $\text{Fe}(\text{III})$ -catalysed decomposition of H_2O_2 . While in Fenton-like treatment only the highest molar ratio of $\text{TCP}/\text{Fe}^{3+}/\text{H}_2\text{O}_2 = 1/4/40$ results in complete TCP degradation in 90 min treatment time (Fig. 1), the kinetics of TCP removal by $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ is characterized by a more rapid decay without any lag-phase at a four-times lower ratio of $\text{TCP}/\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 1/1/10$ (Table 1).

The organic substrate to be oxidized and its degradation by-products (intermediates) may influence the efficacy of the Fenton-based oxidation process substantially. For example, quinone-structure compounds formed as phenol intermediates and its derivative oxidation shuttles electrons from the HO^\bullet adduct of the starting aromatic compound to Fe^{3+} , thereby facilitating the degradation of starting aromatic compounds [5]. Hydroquinones and catechols are known to reduce Fe^{3+} to Fe^{2+} under acidic conditions and therefore accelerate the production of HO^\bullet by the classical Fenton reaction (Eq. (1)) [5,33]. An estimation of initial Fe^{2+} oxidation rate in the reported conditions using a rate constant value of $53 \text{ M}^{-1} \text{ s}^{-1}$ [4] for Reaction (1) yields a half-life of about 2 min, which is not consistent with a prolonged depletion in the Fe^{2+} concentration profile of the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system (Fig. 2). In addition, slow but remarkable increase of Fe^{2+} was observed after 30 min. Both findings led to the assumption of Fe^{3+} reducing process by TCP degradation intermediates reflecting therefore on Fe^{2+} concentration profile in reaction mixture.

Several researchers have indicated the formation of quinone-, hydroquinone-, and catechol-structure intermediates, as 2,6-dichloro-1,4-benzoquinone, 2,6-dichloro-1,4-dihydroxybenzene, and 3,5-dichlorocatechol, during TCP degradation by the advanced oxidation (in particular, the Fenton-like process) [34,35,43]. Thus, it is reasonable to assume the multiple-step oxidation mechanism

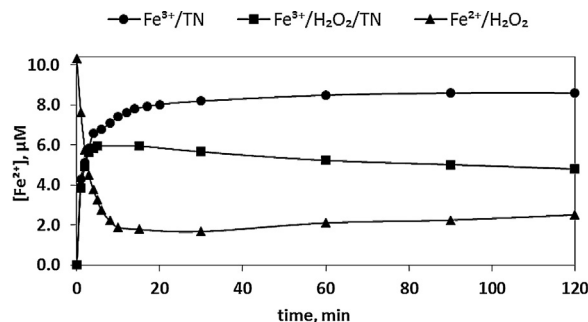


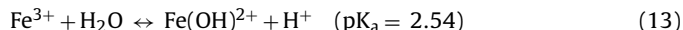
Fig. 2. Concentration profile of Fe^{2+} (μM) during degradation of TCP by Fe^{3+}/TN , $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{TN}$, and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$. $[\text{TCP}]_0 = [\text{Fe}^{2+}]_0 = [\text{Fe}^{3+}]_0 = 10 \mu\text{M}$, $[\text{H}_2\text{O}_2]_0 = 100 \mu\text{M}$, $[\text{TN}]_0 = 10 \text{ mg L}^{-1}$.

of TCP by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ with an initial oxidation step characterized by a slow TCP degradation rate (lag-phase) (Eqs. (1) and (9)–(12)) and a subsequent acceleration (Table 1) provided by the reaction (Fe^{3+} reduction and electron transport) of intermediates.

No TCP degradation by unaccompanied H_2O_2 treatment resulted.

3.2. Formation and reactivity of Fe^{3+} -TN complexes in catalytic decomposition of TCP by Fenton-based process

The addition of TN, a major constituent of the real wastewater, to the reaction mixture increased the degradation rate of TCP by the $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system substantially (Table 1). The role of TN in activation of the H_2O_2 oxidation by Fe^{3+} can be explained by its molecular structure (Fig. 3), which consists of several monomers of gallic acids attached to each other by depside bonds, or to a central polyol (such as glucose) by ester bonds [44]. Gallic acid is known to form unstable complexes with Fe^{3+} , which then decay by electron transfer. In aqueous solutions, $\text{Fe}(\text{OH})^{2+}$ (Eq. (13)) is a dominant species of Fe^{3+} -hydroxo complexes at pH 3.0 [45].



According to the investigation of Hynes and Coinceannainn [46] on the kinetics and mechanism of gallic acid reactions with Fe^{3+} , two complexes of Fe^{3+} with gallic acid, protonated $[\text{Fe}(\text{LH})]^{2+}$ and deprotonated $[\text{Fe}(\text{L})]^+$, are formed from pH 1.0 to 3.0. These complexes then decay through an electron transfer reaction to form Fe^{2+}

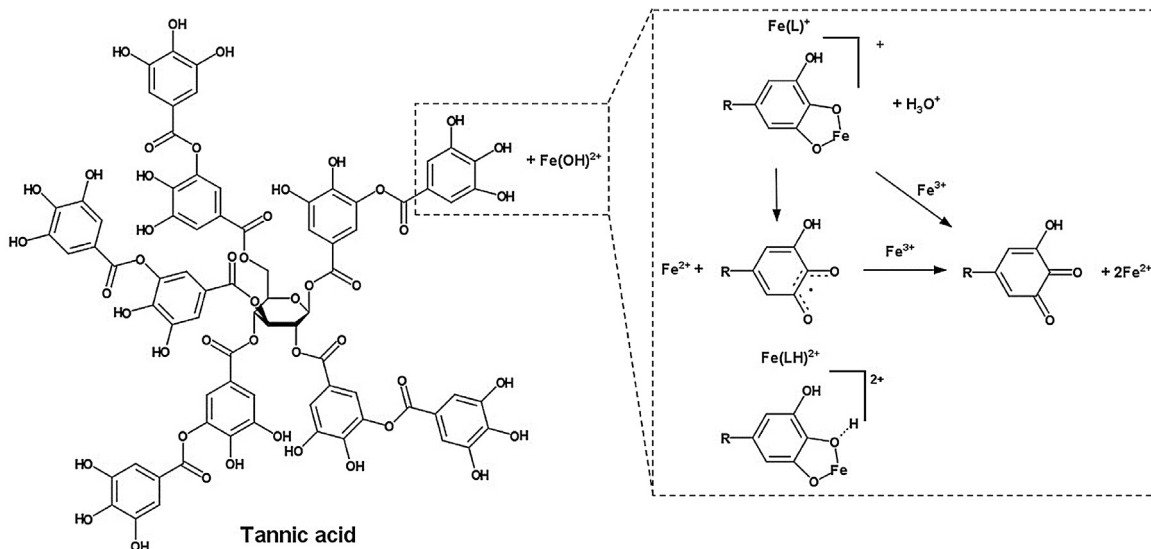


Fig. 3. Proposed mechanism of Fe^{3+} reduction by TN. $\text{Fe}(\text{LH})^{2+}$ and $\text{Fe}(\text{L})^+$ are protonated and deprotonated complexes, respectively.

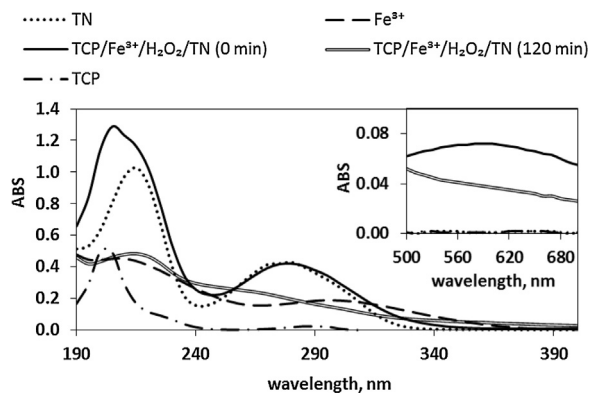


Fig. 4. Light absorption spectra of Fe^{3+} , TCP, TN, and $\text{TCP}/\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{TN}$ reaction system (inset is the enlargement of Fe^{3+} -TN complex absorbance in the $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ treatment system at pH 3.0 in the beginning of the reaction and after 120 min). $[\text{TCP}]_0 = [\text{Fe}^{3+}]_0 = 10 \mu\text{M}$, $[\text{H}_2\text{O}_2]_0 = 100 \mu\text{M}$, $[\text{TN}]_0 = 10 \text{ mg L}^{-1}$.

and the quinone group. Spectrophotometric studies on the complexity of TN with Fe^{3+} at pH 3.0 demonstrated an absorption area of a TN- $\text{Fe}(\text{III})$ complex with its maximum at 580–600 nm (inset of Fig. 4) and TN maximum absorbance at 215 and 280 nm (Fig. 4). In the study by Sungur and Uzar [28], a maximum absorbance of the TN- $\text{Fe}(\text{III})$ complex at pH < 3.0, pH 3.0–7.0, and pH > 7.0 was recorded at 620, 600, and 500 nm, respectively.

The reduction of Fe^{3+} in the $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system in the presence of TN was also confirmed experimentally (Fig. 2). The mass ratio of Fe^{3+}/TN was 1/18 in these experiments. The theoretical stoichiometric ratio of Fe^{3+}/TN for the complete reduction of Fe^{3+} cannot be calculated because of the polymeric structure of TN and the uncertain number of bounded gallic acid monomers. According to the spectrophotometric investigations, Fe^{3+} was at least partially complexed by TN at the beginning of the treatment and was still present in the solution at lower concentration after 120 min treatment (the absorbance of the $\text{Fe}(\text{III})$ -TN complex was reduced; see inset of Fig. 4). The Fe^{2+} concentration profile in $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{TN}$ indicated the competitive reactions of Fe^{3+} reduction by TN and H_2O_2 oxidation of Fe^{2+} mediated by the Fenton chemistry (Eqs. (1), (4), and (6)). The concentration of Fe^{2+} was reduced from 5.9 to 4.8 μM within 15–120 min. In addition, competitive reactions of $\text{Fe}(\text{III})$ -TN complex formation and TN oxidation occurred. Spectrophotometric analysis showed a substantial decrease in TN absorbance (Fig. 4) and TN- Fe^{3+} complex (500–700 nm) absorbance after 120 min of H_2O_2 oxidation (inset of Fig. 4). Some extension of TN peak (λ to 400 nm) absorbance indicated structural changes of TN molecules attacked by oxidative species (HO^\bullet , HO_2^\bullet). Kalyanaraman et al. [25] found that TN was degraded effectively by the Fenton treatment with the formation of low molecular weight compounds. Fragments of gallic acid, catechin, $\text{C}_8\text{H}_8\text{O}_2$, and $\text{C}_9\text{H}_{12}\text{O}$ were observed in gas chromatographic spectrometric analysis. This also explains the difference in concentration of Fe^{3+} reduced by TN in the presence and absence of H_2O_2 ($\text{Fe}^{3+}/\text{TN}/\text{H}_2\text{O}_2$ and Fe^{3+}/TN , Fig. 2).

In addition to TN degradation, which was confirmed indirectly by spectrophotometric studies, an increased consumption of H_2O_2 in the $\text{TCP}/\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{TN}$ reaction mixture was observed (Fig. 5). A 120 min treatment time was required for near-complete degradation of TCP by applying higher dosages of H_2O_2 ($[\text{H}_2\text{O}_2]_0 = 400 \mu\text{M}$) and TN ($[\text{TN}]_0 = 50 \text{ mg L}^{-1}$) and lower dosages of H_2O_2 ($[\text{H}_2\text{O}_2]_0 = 100 \mu\text{M}$) and TN ($[\text{TN}]_0 = 10 \text{ mg L}^{-1}$) (Fig. 6). This indicates an excessive consumption of H_2O_2 with regards the target compound. Although elevated dosages of H_2O_2 are of necessity in case of higher concentration of TN, the reciprocal removal of TN (toxic constituent of water) and H_2O_2 (toxic oxidising chemical) is of a practical importance.

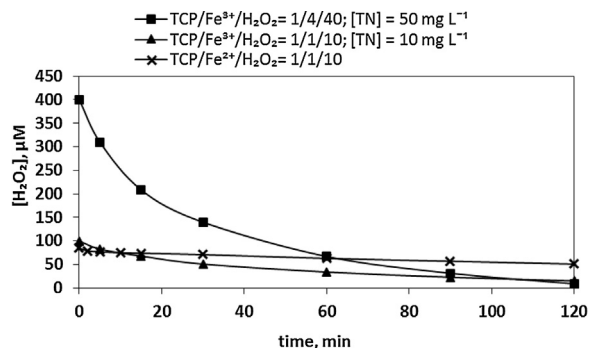


Fig. 5. H_2O_2 consumption during TCP treatment by $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{TN}$ and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$. $[\text{TCP}]_0 = 10 \mu\text{M}$, $[\text{H}_2\text{O}_2]_0 = 100$ or $400 \mu\text{M}$, $[\text{Fe}^{3+}]_0 = 10$ or $40 \mu\text{M}$, $[\text{Fe}^{2+}]_0 = 10 \mu\text{M}$, $[\text{TN}]_0 = 10$ or 50 mg L^{-1} .

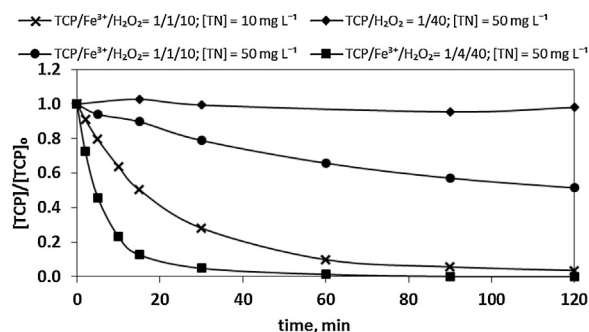


Fig. 6. TCP degradation by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ within 120 min treatment in the presence of TN. $[\text{TCP}]_0 = 10 \mu\text{M}$, $[\text{Fe}^{3+}]_0 = 10$ or $40 \mu\text{M}$, $[\text{H}_2\text{O}_2]_0 = 100$ or $400 \mu\text{M}$, $[\text{TN}]_0 = 10$ or 50 mg L^{-1} .

Thus, similar to that found in biological systems [30,31] TN in Fenton-based contaminated water treatment possesses antioxidant properties—as a hydroxyl radical scavenger that is autocatalytically degraded—and pro-oxidant properties—as a Fe^{3+} reductant. That should result in the effective purification of pulp and paper industry effluent, where, besides chlorophenols, TN is among the major constituents requiring degradation.

3.3. TCP degradation by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ in the presence of TN

TCP degradation in the presence of TN followed pseudo-first order reaction kinetics with a multiple-step reaction mechanism. Contrary to results obtained in the kinetic study of the $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system, the degradation of TCP in the presence of TN proceeded without any lag phase in the first step with a higher pseudo-first order reaction rate constant of TCP degradation than in the second one (Table 1). TCP degradation was only slightly slower by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ in the presence of TN than by the classical Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2 = 1/10$).

Contrary to our previous study [9], where ascorbic acid—another Fe^{3+} reductant—was able to degrade the target pollutant by HO^\bullet (generated from H_2O_2 through direct electron transfer and proton donation from the ascorbate anion to H_2O_2 with its subsequent decomposition to HO^\bullet) independent of mediation by transition metals, TN addition to H_2O_2 alone resulted in no TCP oxidation (Fig. 6).

Expected HO^\bullet formation was observed in $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ with the addition of TN. Instantaneous formation of HO^\bullet in $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ (Fig. 7) and the relatively fast release of reduced Fe^{2+} in $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{TN}$ (Fig. 2) implied an unexpected decrease in HO^\bullet concentration by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ in the presence of TN. The unsubstantial delay in TCP degradation by $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{TN}$ (Table 1) and the decrease in HO^\bullet concentration compared to $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ (Fig. 7) could be explained

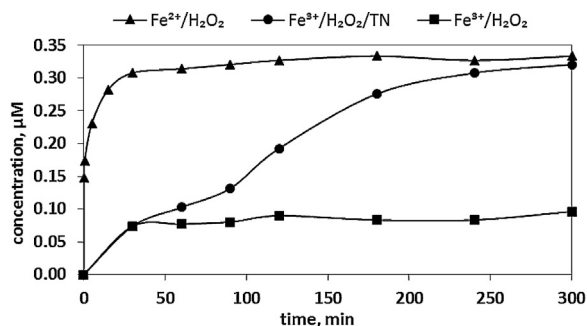


Fig. 7. Formation of hydroxyl radicals in $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{TN}$, $\text{Fe}^{3+}/\text{H}_2\text{O}_2$, and $\text{Fe}^{2+}/\text{H}_2\text{O}_2$. $[\text{Fe}^{3+}]_0 = [\text{Fe}^{2+}]_0 = 10 \mu\text{M}$, $[\text{H}_2\text{O}_2]_0 = 100 \mu\text{M}$, $[\text{TN}]_0 = 10 \text{ mg L}^{-1}$.

by the HO• scavenging properties of TN. Although TN scavenged HO• and resulted in the considerable H_2O_2 consumption (Fig. 5), the degradation of TN is among the benefits of the treatment, as TN is a major constituent of the water requiring degradation.

Structure of TN hypothetically can yield organic radical species. According to the study of Fukushima and Tatsumi [24] such organic radical formation can result in the incomplete dechlorination of TCP, because the chlorinated species from TCP are able to bind to TN. Therefore, dechlorination of TCP after 120 min of the treatment by $\text{Fe}^{3+}/\text{H}_2\text{O}_2$, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{TN}$ was evaluated. Both treatment systems, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{TN}$, resulted in close dechlorination of 82 and 78% (of theoretical maximum formed Cl^-), respectively, while the treatment with $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ allow to achieve only 2% of dechlorination. 24.6, 23.3 and $0.5 \mu\text{M}$ of Cl^- in $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{TN}$ and $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ were formed, respectively. This indicated that the addition of TN to $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ was effective for dechlorination in TCP degradation.

After 300 min, the HO• production level was equal to that of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$, which indicates that the Fe^{3+} -reducing properties of TN propagate HO• formation. HO• production in $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{TN}$ was substantially higher than that in the Fe^{3+} -mediated H_2O_2 system without TN, which supports the assumption that TN is able to boost the Fenton reaction. HO• was not detected in reaction solutions that contained sole TN, H_2O_2 , Fe^{2+} or Fe^{3+} .

Thus, the observed reduction of Fe^{3+} , HO• formation along with H_2O_2 consumption, and rapid TCP degradation with high dechlorination support the ability of TN, despite its radical scavenging properties, to boost the Fenton-based process utilising Fe^{3+} as a catalyst of H_2O_2 oxidation. A similar chlorophenol transformation route may occur in the natural environment since (1) chlorophenols [13] and tannins [18] are formed by natural transformation routes and exist in natural water; (2) transition metal-reductive properties of tannins in natural water have been observed [18]; and (3) H_2O_2 and Fe^{2+} found in natural water [47,48] may initiate Fenton-based processes.

The results demonstrated TN participation in the iron ion redox cycling and as the consequence improved Fenton-based oxidation of contaminants in water.

3.4. Ferric sludge for catalytic decomposition of TCP by Fenton-based process in the presence of TN

Under strongly acidic conditions without H_2O_2 and complexing agents, Fe(III) exist as the hexaquo ion $\text{Fe}(\text{H}_2\text{O})_6^{3+}$. With increase in pH, the hexaquo ion of Fe^{3+} (Eq. (14)) undergoes extensive hydrolysis with amorphous ferric oxyhydroxide precipitation [49].

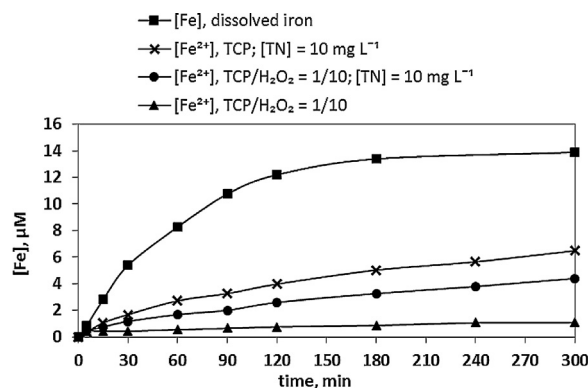
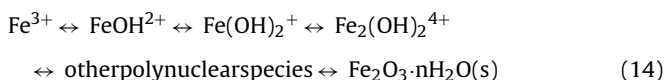


Fig. 8. Effect of TN on iron dissolution in 50 mg L^{-1} ferric sludge suspension and on Fe^{3+} reduction of sludge in H_2O_2 treatment of TCP. $[\text{TCP}]_0 = 10 \mu\text{M}$, $[\text{H}_2\text{O}_2]_0 = 100$ or $400 \mu\text{M}$.

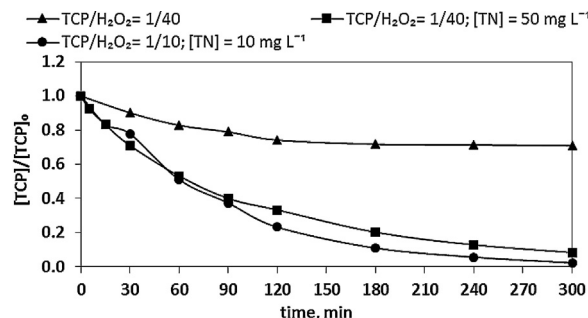


Fig. 9. Degradation of TCP by H_2O_2 in 50 mg L^{-1} ferric sludge suspension within 300 min of H_2O_2 treatment in the presence and absence of TN. $[\text{TCP}]_0 = 10 \mu\text{M}$, $[\text{H}_2\text{O}_2]_0 = 100$ or $400 \mu\text{M}$.

TCP removal by H_2O_2 oxidation with ferric sludge similarly to the $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ and $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ systems followed pseudo-first order reaction kinetics (Table 1). TCP degraded slower by H_2O_2 oxidation activated by ferric sludge than by Fe^{3+} because of the additional reaction of iron dissolution in aqueous media (Fig. 8). The reaction rate was accelerated substantially in the presence of TN (Table 1) resulting in a near-complete degradation of TCP in 300 min (Fig. 9). This confirmed the need for organic reductants in water treated by the Fenton with ferric sludge reuse. A lower dosage of TN (10 mg L^{-1}) and H_2O_2 ($\text{TCP}/\text{H}_2\text{O}_2 = 1/10$) favoured TCP degradation by the H_2O_2 -ferric sludge system. A higher dosage of TN required a higher addition of H_2O_2 because of the competitive oxidation reactions of TCP and TN. Thus, H_2O_2 dose and ferric sludge load for water treatment in the presence of TN should be optimized to balance Fe^{3+} reduction to boost the Fenton reaction and HO• scavenging to remove TN from water.

Acidic reaction media (pH 3.0) and the presence of TN (solute) with chelating and reducing properties may result in three main iron dissolution mechanisms: protonation, complexation, and reduction [6,50–53].

Acidic media favoured iron dissolution by protonation. This mechanism relies on protons (H^+) binding with an OH-group on the hydrated substrate surface (step 1, Fig. 10a). This reaction then weakens the Fe–O bond in ferric oxyhydroxide with slow detachment of surface Fe(III) species into solution (step 2, Fig. 10a).

Dissolution by complexation involves the attachment of a chelating compound (TN) onto the ferric oxyhydroxide crystal surface (step 1, Fig. 10b). Deprotonation is required prior to adsorption, since strongly complexing ligands (TN) in the solution exchange for a protonated OH-group bound to the substrate (ferric oxyhydroxide). The surface ion–ligand complex ultimately detaches into the

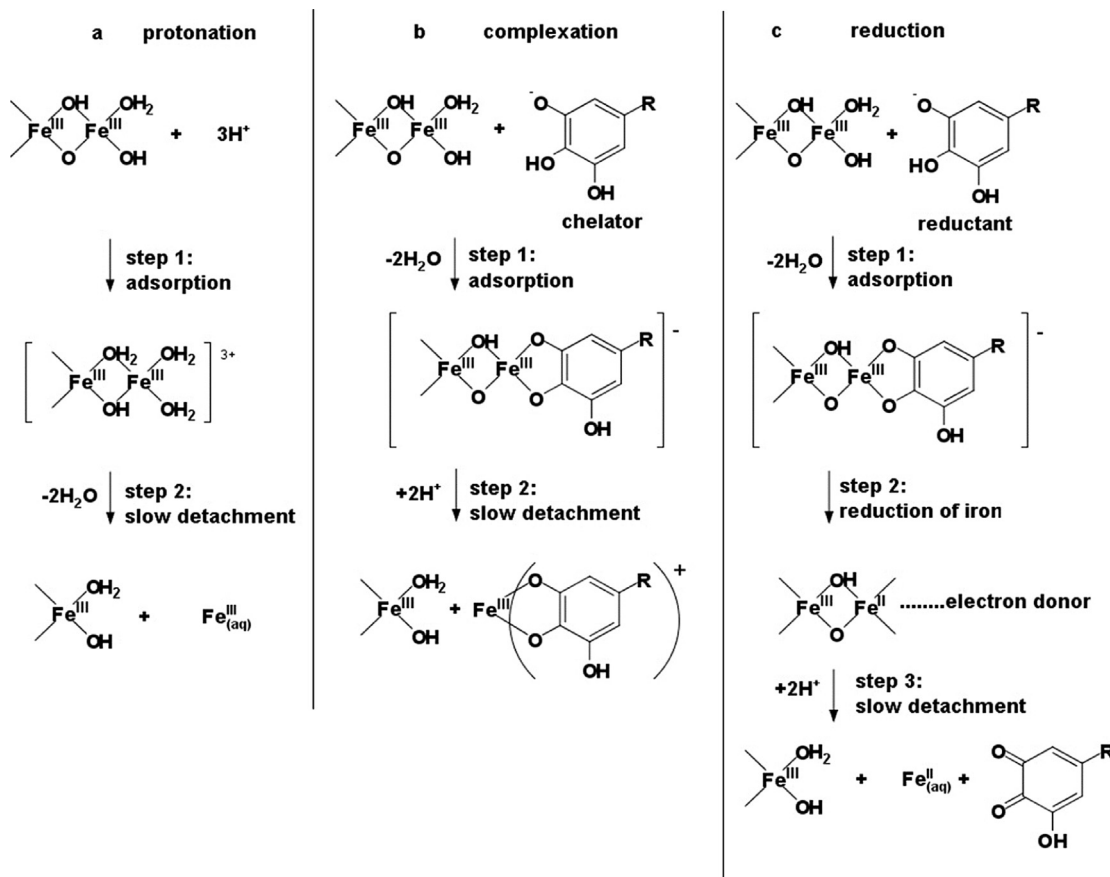


Fig. 10. Iron dissolution mechanisms from ferric sludge: (a) protonation under acidic conditions, (b) complexation, and (c) reduction in the presence of gallic acid (monomer of TN) (R is a rest structure of TN).

aqueous phase (step 2, Fig. 10b). In ferric oxyhydroxide, the high polarity of the surface complex leads to a decrease in bond strength between the surface iron and its neighbouring atoms that facilitates iron dissolution.

Dissolution by reduction implies that the Fe(III) sites on the substrate (ferric oxyhydroxide) surface gain an electron from the adsorbed solute (electron donor) and are reduced to Fe(II) (step 2, Fig. 10c). The newly formed Fe(II) at the substrate surface has a less stable bond with oxygen than its predecessor Fe(III), thus the Fe(II) is more easily detached from the surface than Fe(III) (step 3, Fig. 10c).

Since protons in the phenolic OH-groups of gallic acid (TN monomer) have pKa of 8.7, 11.4, and above 13 [54], the extent of TN dissociation at pH 3.0 was small and TN was mostly present in solution in undissociated form. Since TN deprotonation is required prior to complexation (Fig. 10b) and reduction (Fig. 10c), the probability of iron dissolution from ferric sludge by these mechanisms is very small. Thus, the most evident mechanism of iron dissolution at pH 3.0 is ferric oxyhydroxide protonation with Fe(III) release to aqueous solution (Fig. 10a) followed by Fe(III) reduction to Fe(II) by TN through Fe(III)-TN complex formation with decay by electron transfer reaction mechanism (Fig. 3). The enhanced release of Fe²⁺ from ferric sludge to solution in the presence of TN was observed (Fig. 8). A slightly lower concentration of Fe²⁺ in the ferric sludge/H₂O₂/TN system (Fig. 8) existed because of the utilization of Fe²⁺ for the activation of H₂O₂ oxidation (Eq. (1)) with an effective degradation of TCP (Fig. 9). Adsorption of TCP on the surface of ferric sludge was not observed after 300 min of the solution mixing at pH 3.0.

A study of chlorophenol-contaminated soil treatment [55] showed that organic substances in soil produced by plants and

microorganisms may dissolve iron from natural soil iron minerals, reduce it to Fe²⁺, and boost the reactivity of H₂O₂ oxidation. These findings support results obtained in this study on H₂O₂ oxidation activation by ferric sludge reuse. In soil, Fe²⁺ addition was unnecessary for H₂O₂ decomposition if a considerable amount of reduced metal ions was present; the reductant availability in wastewater allows for the reuse of non-regenerated ferric sludge for Fenton-based oxidation without any supplementary Fe²⁺.

4. Conclusions

H₂O₂ oxidation activated by Fe²⁺ resulted in a considerably higher degradation rate of TCP than that catalysed by Fe³⁺. The addition of TN accelerated the degradation rate of TCP and substantially improved the dechlorination by the Fe³⁺/H₂O₂ system substantially. TN exhibited Fe³⁺-reductive properties and boosted the reactivity of the Fenton-based process towards TCP degradation by improving iron redox cycling and as a result enhanced activation of H₂O₂ oxidation. Along with the degradation of TCP the scavenging of the hydroxyl radicals by TN was observed. This is not a limitation, since TN is a major constituent in water to be degraded. Among the benefits is that TN degradation proceeded along with the removal of unconsumed by TCP H₂O₂. Thus, H₂O₂ and Fe³⁺ dosages should be optimized to maintain both properties of TN to reduce ferric iron and to scavenge the HO[•]. Iron dissolution from ferric sludge and its reduction by TN to Fe²⁺ was observed under acidic conditions. This improved the reactivity of the Fenton-based process with ferric sludge as the catalyst source of the H₂O₂ oxidation.

The study indicated that natural water or wastewater constituent, TN, is involved in the Fenton chemistry and supports

the reuse of ferric sludge as a catalyst source of H_2O_2 oxidation. As a result, expenses of Fe^{2+} addition and sludge utilization can be minimized. The study demonstrated tannic acid participation in the iron ion redox cycling and as a consequence the improved Fenton-based oxidation of contaminants in water with the effective ferric sludge reuse. This presents a high-impact contribution to Fenton-based treatment of wastewater that may result in increased treatment efficacy, and decrease in solid waste accumulation and treatment cost.

Acknowledgement

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